

Communicating Research to the General Public

At the March 5, 2010 UW-Madison Chemistry Department Colloquium, Prof. Bassam Z. Shakhashiri, the director of the Wisconsin Initiative for Science Literacy (WISL), encouraged all UW-Madison chemistry Ph.D. candidates to include a chapter in their Ph.D. thesis communicating their research to non-specialists. The goal is to explain the candidate's scholarly research and its significance to a wider audience that includes family members, friends, civic groups, newspaper reporters, program officers at appropriate funding agencies, state legislators, and members of the U.S. Congress.

Over 50 Ph.D. degree recipients have successfully completed their theses and included such a chapter.

WISL encourages the inclusion of such chapters in all Ph.D. theses everywhere through the cooperation of Ph.D. candidates and their mentors. WISL is now offering additional awards of \$250 for UW-Madison chemistry Ph.D. candidates.



The dual mission of the Wisconsin Initiative for Science Literacy is to promote literacy in science, mathematics and technology among the general public and to attract future generations to careers in research, teaching and public service.

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Development of Novel Surface Sensitive and Surface Specific Two-Dimensional Spectroscopies

By

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Appendix

Summary to General Public

To explain my research to a broad, non-scientific audience I have written this chapter to be included in my PhD dissertation. The goal of scientific research in general is to understand the world around us. A major driving force behind this goal is that this understanding of the world will be useful to many people. Thus, it is imperative that we communicate our scientific findings with others. It is our responsibility as scientists to share the knowledge we learn not only with our colleagues, but with the general public. I want to thank the Wisconsin Initiative for Science Literacy at UW-Madison for providing me this opportunity to engage in such scientific communication. The creation of this chapter could not have been possible without their sponsorship and support.

Have you ever been at the beach and forgotten your sunglasses? The glare of the sun off of the water seems to meet your every gaze. This blinding light seems to be directed right at you. If only you had remembered your sunglasses! With this simple accessory you could look out across the beautiful beachfront, your line of sight unobstructed by any intense rays. Coincidentally, a lot of the questions I have focused on in my PhD start here, at the beach, without my sunglasses. When at the beach, we might wonder why does this glare happen in the first place? But in the lab, the question is how does light interact with a surface? At the beach we might ask, why do sunglasses help reduce this glare? But in the lab we are curious about how manipulating that light changes its interactions with a surface? No matter where we are, at the beach or in the lab, how might we learn about this surface through interactions with light? It is this last question that I strived to answer in

my research by using a technique called two-dimensional (2D) spectroscopy. Spectroscopy is the study of matter through measuring a spectrum produced by that matter interacting with light. Two-dimensional spectroscopy requires multiple of these light and matter interactions to produce a spectrum that contains more information than can be gleaned by just one interaction. To be more precise, 2D spectroscopy provides unique characteristics related to the structural and dynamics of the matter being investigated. For example, 2D spectroscopy has measured how proteins fold over time as well as the dynamics of charge separation within solar cell material.

To accomplish these experiments, we first need light. At the beach, the sun is the light source and the light from the sun is unpolarized. Light is an electromagnetic wave that travels along different planes. Unpolarized light means that the wave propagates in multiple planes simultaneously and takes up space in all three dimensions. When this unpolarized light from the sun hits the surface of the water, it becomes polarized, meaning that it is now traveling in one plane. The glare we experience at the beach is this polarized light that has bounced off of the surface of the water. To reduce this glare, we dig into our beach bags and put on a pair of sunglasses. But not just any sunglasses, we use polarized sunglasses. The lenses that make up this pair of sunglasses are made from an absorptive polarizing material, known as polyvinyl alcohol. In making these lenses, the material is stretched to align the polyvinyl alcohol molecules in one direction. When light hits the lenses of your sunglasses, the light that is traveling in the same direction as the aligned polyvinyl alcohol molecules is absorbed by these molecules, while the rest is transmitted. Your polarized sunglasses effectively filter out the glare from the surface of the water (Fig. A.1).

In the lab, the light source we use is a laser. Instead of having a continuous source of light (like sunlight), the laser is pulsed, meaning that light is produced at a specific repetition rate. For 2D spectroscopy, we use ultrafast lasers that commonly operate at 1 kHz (1000 pulses per second) but can also be used at higher repetition rates. Moreover, these pulses are very precisely defined in time, around 100 femtoseconds, or approximately 10^{12} times faster than the shutter speed of a smartphone camera. Having ultrashort pulses in time allows us to probe dynamics of matter that occur at this time scale. But what types of matter do we care about? For my research, I have focused

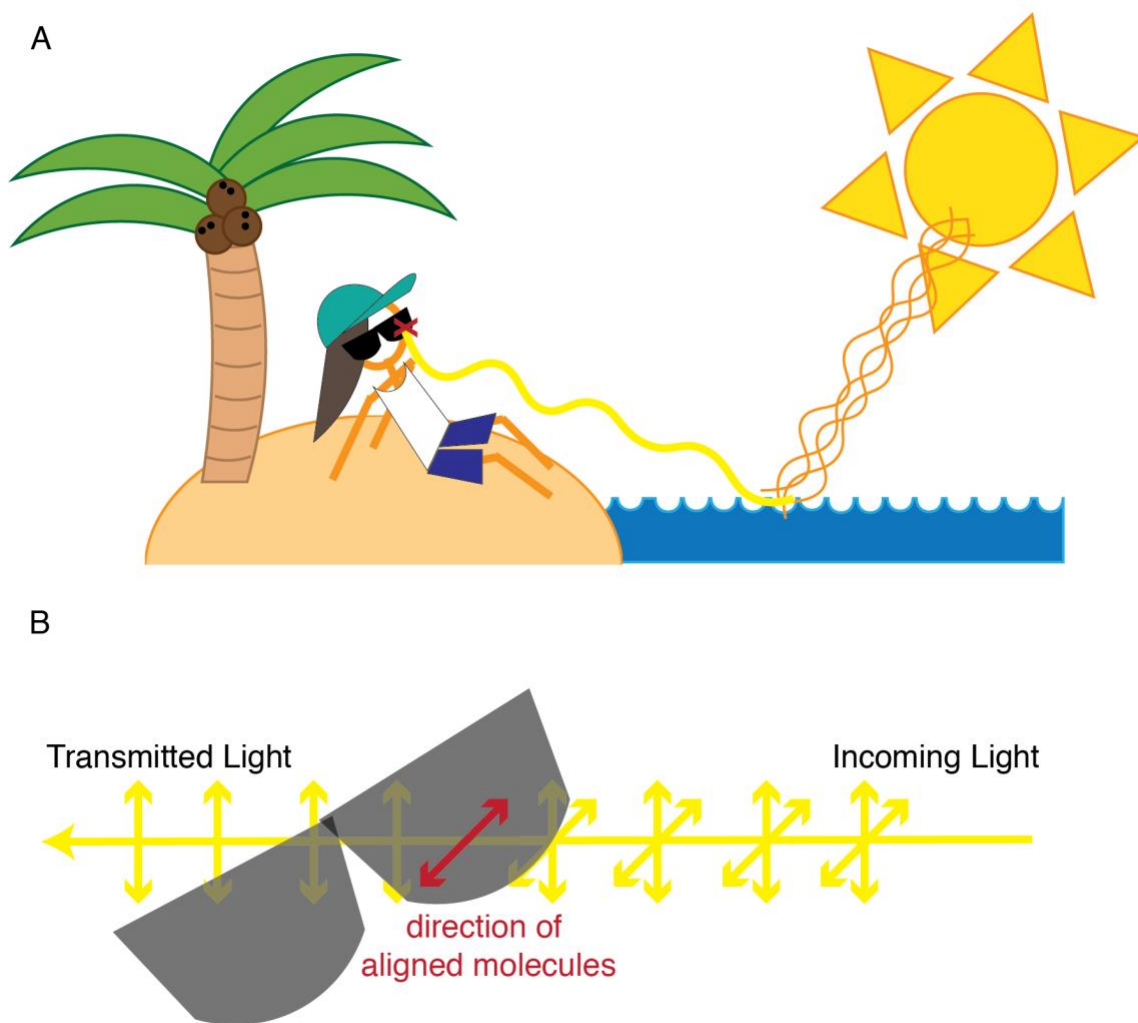


Figure A.1 A) A schematic of myself, at the beach, wearing polarized sunglasses that are blocking the harsh reflection of the sun's rays from the water's surface. B) A depiction of how polarized sunglasses work.

on materials on surfaces that have ranged from small molecules on a surface, to proteins, and even

molecular crystals (a solid material made from repeating copies of a molecule in a specific pattern). The goal of my research projects is to develop new ways to use 2D spectroscopy to learn about the structure of these molecules on a surface.

My PhD research has focused on two different methods to improve the study of surfaces with 2D spectroscopy. The first employs techniques that enhance the signals of molecules at a surface. In most surface systems, whether they be chemical, biological, or material systems, there are relatively few molecules present on the surface. Therefore, before we can learn about the structure of molecules on a surface, we first have to be able to detect a signal from the molecules that are present. I accomplish this by first changing the surface our molecules are on as well as changing the direction we collect the signal. I will discuss these changes in further detail below. The combination of these two tricks enhances the signal observed from the light-molecule interaction at the surface and provides 2D spectroscopy a way to measure the characteristics of a very small amount of molecules.

In this first project, the samples under investigation were inherently surface samples. They contained a single layer of molecules tethered to a surface (Fig. A.2A). But what about systems where there are not only a single isolated layer of molecules at a surface, but molecules in a solution on top of that surface (Fig A.2B)? In other words, what about an interface between two types of materials? Such as when oil is on water, or water droplets on glass? How can we learn about what is happening where these two materials meet? How can we measure characteristics of the small number of molecules at the boundary of these two materials? The goal of my second project was to develop a method that was able to accomplish measurements of these types of interface systems (Figure A.2B) with 2D spectroscopy. With this interfacial system in mind, I developed a method that relies on controlling the polarization of light both before and after the light hits the surface.

By controlling the polarization of light both before and after, we are able to solely probe the structure of molecules from an ordered surface without measuring signals from molecules that make up the bulk. If we could bring our lab to the beach, we could perform this same experiment

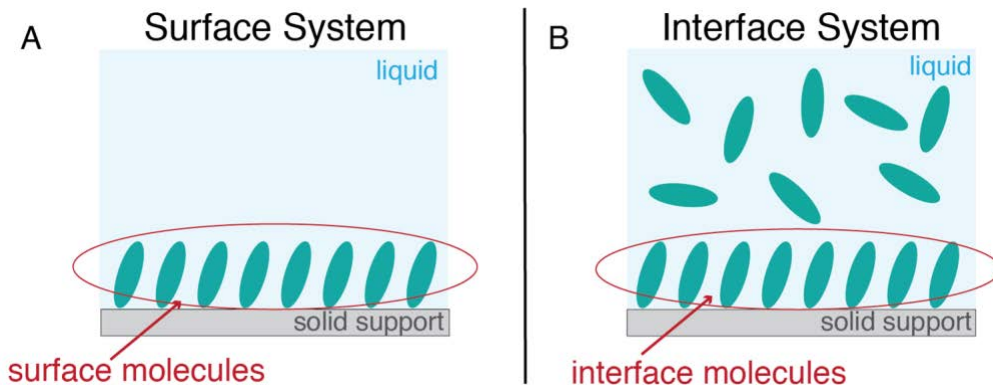


Figure A.2 A) A model surface system. B) A model interface system.

on the ocean.

By controlling

the

polarization

of light, we

could measure

the molecules

on the surface of the water, without measuring any signals from what stirs beneath the waves.

Back at the beach, we cannot change how the sunlight hits the ocean's surface. We cannot change its polarization, or the angle at which the light hits the water, or the water itself. But in the lab, we have control over all these parameters. By choosing how to manipulate the light and surface interactions, I have been able to develop novel methods for 2D spectroscopy to measure characteristics of molecules at surfaces.

A.1 INTRODUCTION TO TWO-DIMENSIONAL SPECTROSCOPY

What makes the polarizing sunglasses so effective at blocking the glare at the beach is the fact that molecules that make up the lens absorb light. But what does it mean to absorb light? Light is energy, and when it interacts with molecules, some of that energy is passed onto the molecules in some way. How the molecule dissipates that energy depends on the wavelength, or frequency, of light used. For example, if microwaves are used (such as in your microwave at home), the

wavelength of light causes the molecular bonds to rotate, just like a spinning top. If infrared light (light beyond the red part of the visible light spectrum) is used, the molecular bonds oscillate, like

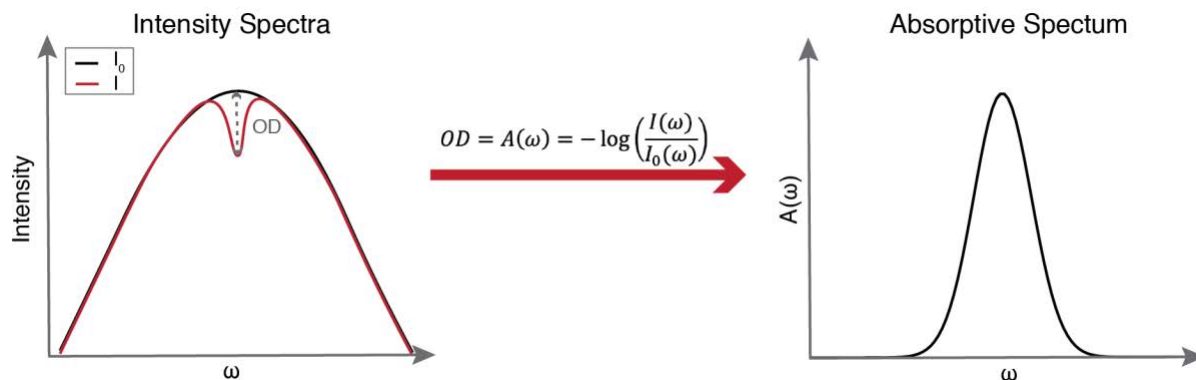


Figure A.3 Depiction of the light intensity before, I_0 (black line), and after, I (red line) going through a sample. This intensity is plotted as a function of the energy of light in frequency (ω). The absorptive spectrum is then calculated based on this change in

when a spring is pulled and then let go of. If visible light is used, the electrons that make up the molecule are displaced from their original state to one with higher energy. All of these processes follow the law of conservation of energy such that the total amount of light (or energy) put into the system must equal the light that comes out of the system plus any energy that is imparted to the molecules. It is this energy that is imparted to our molecules of interest that we wish to measure, as it provides characteristic information on the molecules themselves. However, measuring it directly is very difficult. So instead, we measure the light before and after it interacts with the molecular system. If we monitor the light going in and compare it to the light coming out after it interacts with a molecule, the intensity of the light decreases. Figure A.3 demonstrates this by visualizing the intensity of light before (black line) and after (red line) it interacts with a molecule. The dip in Figure A.3, or loss of light, is what we refer to as absorption. The amount of loss and the frequency at which this loss of light occurs provides information on the molecules under investigation. The amount of light loss, or the strength of the absorption of the molecules, is termed the optical density (OD). It is this quantity that is measured in absorption spectroscopy. To produce a positive absorption spectrum, we use a formula that accounts for the intensity of light both before

and after the sample. In general, because there is only one light-matter interaction in this type of spectroscopy, it is referred to as linear absorption spectroscopy.

In my work, instead of looking at the absorption of light after one light-matter interaction, we instead use multiple light-matter interactions. We refer to these as the pump and probe light pulses. The pump pulse puts energy (via light) into our system, while the probe pulse interrogates where that energy has gone after some amount of time. The role of the pump and probe pulses are like what happens in a game of hide and seek. The pump pulse inputs energy that causes the system to respond, or in the case of the game causes people to go hide. Sometime later, the probe pulse comes to measure that response, or in the game the seeker goes and finds where the people are

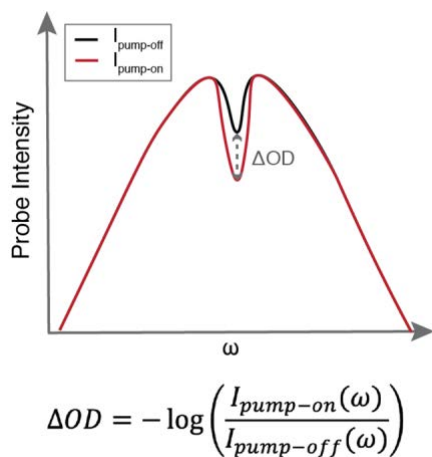


Figure A.4 Depiction of the definition of OD measured using 2D spectroscopies. The black line is the probe light pulse when the pump is off, while the red light is the probe light pulse when the pump is on.

hiding. In practice, we measure how the intensity of the probe light changes when the pump light is on versus off (Fig. A.4). This is called the delta optical density (ΔOD). To achieve a change in the optical density of the molecule, the pump pulse interaction induces the absorption of light. This change in the intensity of light is just like above when we only had one light-matter interaction. Thus, the pump creates a dip in the intensity of our light (OD). Our probe pulse interacts with the molecules and creates further changes to this optical density. It is this difference that is the ΔOD and is what we measure in nonlinear absorption

spectroscopy (Fig. A.4). Doing so provides more information about the molecules we care about by allowing us to probe how different parts of the molecules that absorb light (termed molecular

absorbers) are connected. This connection can tell us about how energy is being transferred between different parts of the molecule and how the molecular structure may be changing over time in response to the interrogation by light. We call this connection coupling, as it tells us about

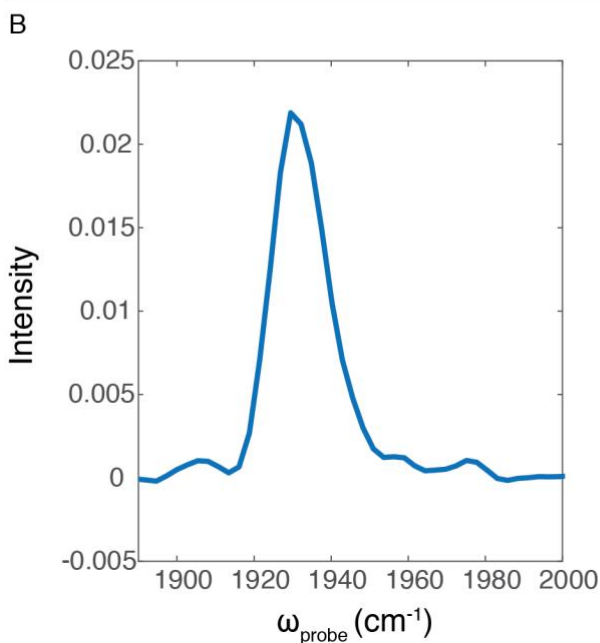
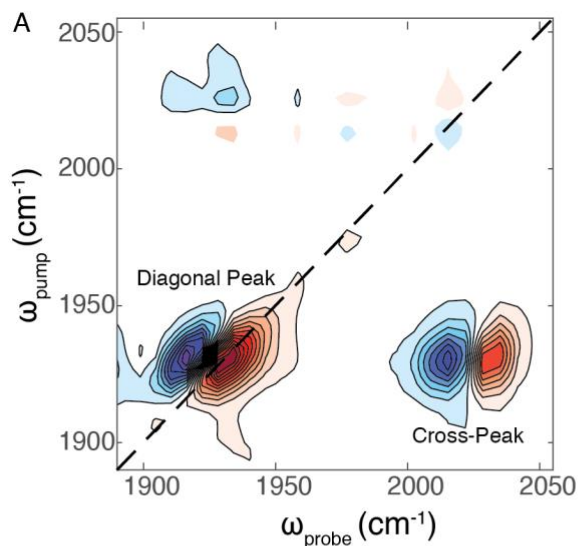


Figure A.5 A) A 2D IR spectrum of a rhenium metal carbonyl. Both a diagonal and cross-peak are observed. B) A diagonal slice through the dashed line in (A).

how different energy states within the molecule are related or “coupled” together. Think of an old married couple walking through a park holding hands. If one of the two stops to admire a flower, while the other continues on, the two separate as tension is formed across their hands. In other words, the actions of one has affected the other because they are connected through their “coupled” hands.

To visualize the ΔOD , we plot the frequency of the light of the pump vs. the frequency of light of the probe. We create a two-dimensional plot of the energy landscape of the molecules under investigation. An example of a 2D spectrum generated this way is shown in Figure A.5A.

From the spectrum, we can see two types of peaks, diagonal peaks and cross-peaks.

These peaks are labeled in figure A.5A. If we take a cut of this spectra along the diagonal (Fig.

A.5B), we get a spectrum that looks very similar to the absorptive spectrum shown in Figure A.3B. The cross-peaks occur at places off the diagonal. The presence of a cross-peak in the 2D spectrum tells us that the absorption features on the diagonal are coupled together. In other words, two parts of the molecule that are absorbing light are linked together. The intensity of the cross-peak tells us how strong the link is. The strength of the coupling provides more information on the structure of the molecules under investigation. These cross-peaks are a signature of 2D spectroscopy and cannot be probed by traditional linear absorption spectroscopy.

The type of spectroscopy where multiple light interactions are used to interrogate a material is termed nonlinear spectroscopy. There are many different types and forms of nonlinear spectroscopy, but in my PhD I have focused on two-dimensional infrared spectroscopy (2D IR). When infrared light is used to probe molecules, the wavelength of that light induces vibrations of molecular groups at specific frequencies. These frequencies provide a fingerprint that tells us what type of atoms the molecule is composed of and how these atoms are connected to make that molecule. Thus, the infrared absorption spectra of a molecule contains unique characteristic features specific to that molecule.

A.2 ENHANCING THE SIGNAL STRENGTH FROM MOLECULAR MONOLAYERS FOR 2D IR SPECTROSCOPY

While over the past 20 years 2D IR spectroscopy has been implemented to study a variety of systems, from proteins (the building blocks of biological matter) to catalysts (small molecules that are apt to react), one system that was difficult to study with the technique was a monolayer of molecules. A monolayer of molecules is one single layer of molecules on a surface. When we compare this type of system to that of a solution of molecules, there are far fewer molecules in the monolayer than in the solution. Thus, there are far fewer molecules that can absorb light and

contribute to the overall OD and ΔOD measured by linear and nonlinear spectroscopies. This makes measuring monolayer systems challenging. To overcome this challenge, I have developed a technique to enhance the absorption signal observed from a monolayer of molecules, as well as reduce the background of the 2D IR measurement that can obscure the signal. The technique is termed surface enhanced attenuated reflection (SEAR) 2D IR and accomplishes the ultimate goal of measuring the structure of a monolayer of molecules.

To provide signal enhancement of the single layer of molecules at the surface, we first modified the surface by adding a thin layer of gold. This gold is only 3 nm thick (about 1/5000th the thickness of a human hair), and automatically forms a rough surface.

This roughness is due to islands of gold nanoparticles connecting together in a haphazard way. When light interacts with these islands of gold, the electrons that make up these atoms oscillate, creating what is called a localized

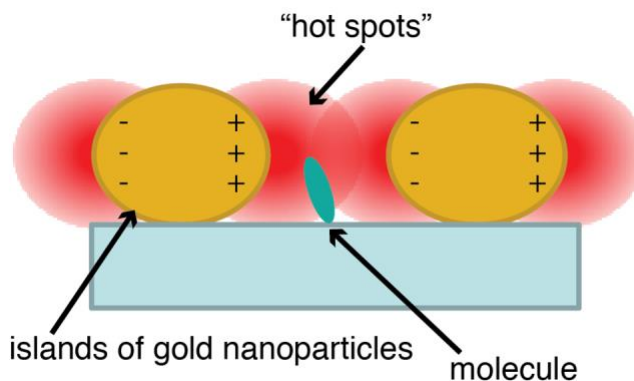


Figure A.6 A cartoon depiction of “hot spots” created between the island of gold nanoparticles.

surface plasmon. This plasmon induces “hot spots” of high intensity electric fields in between the islands of gold (Fig. A.6). When a molecule is located in these hot spots between the islands, it feels a greater intensity of light than what was originally input into the system. This results in more absorption by that molecule, and that ultimately enhances the signal observed. Thus, we are able

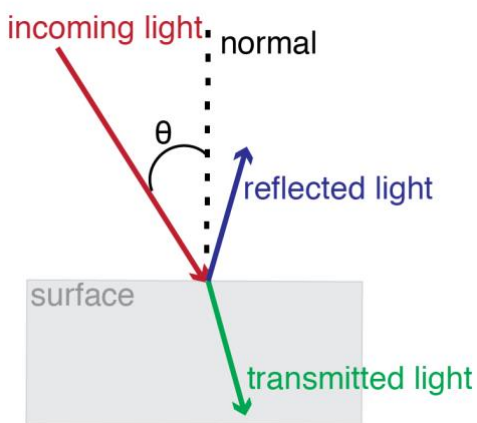


Figure A.7 Schematic of reflected and transmitted light at a surface.

to get around the fact that there are few molecules at the surface and successfully measure a ΔOD of this very thin surface in our 2D IR experiments.

To provide further enhancement to the ΔOD , we combined the use of localized surface plasmons with a reflection geometry as the next step to improve the 2D IR measurement of monolayers. The reflection geometry employs similar physics that light experiences when it is reflected off of the water at the

beach. Whenever light hits an interface at an angle, some of the light is transmitted and some is reflected. Thus when using a reflection geometry, instead of measuring the light after it passes through a surface, we rotate the surface so that the angle between the where the light hits the surface and the surface itself is greater than 90° , and then measure the reflected light (Fig. A.7). Moreover, the amount of light that is reflected versus transmitted depends on the light's polarization.

In general, we consider light to be polarized either vertically or horizontally. More technically, when light hits a surface, we refer to these directions as either p- or s-polarized. P-polarized light refers to light polarized perpendicular to the surface, while s-

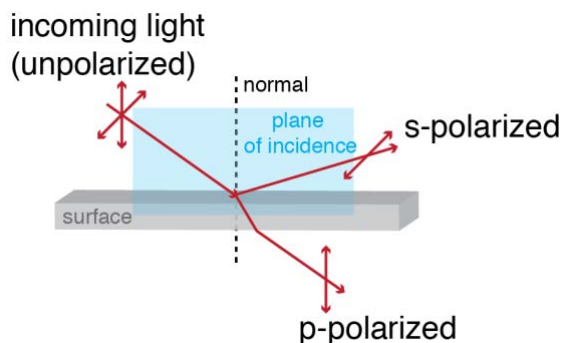


Figure A.8 Definition of s- and p-polarized light relative to a surface.

polarized light refers to light polarized parallel to the surface (Fig. A.8). The amount of light reflected from a surface for both s- and p-polarized light depends on the material of the surface.

For all materials, there is a specific incident angle where the amount of reflected p-polarized light is zero. This angle of incidence where p-polarized light is not reflected is known as Brewster's angle.

Using p-polarized light with an incident angle close to Brewster's angle provides us with an opportunity to enhance the measured ΔOD in our 2D spectrum. Our measurement of ΔOD is based on the change of intensity of the probe light pulse. Ultimately, to produce a greater ΔOD , we would like to reduce the light's intensity after it hits the sample (but not before sample) leading to a higher ΔOD . In our reflection setup, we use p-polarized light and set the incident angle as close to Brewster's angle as possible. By doing this, the amount of reflected light is low, but the same amount of light is still interacting with our surface sample. By collecting the reflected signal light and the small amount of reflected p-light, we have decreased the background we measure our signal against, resulting in an enhanced ΔOD .

By combining this reflection geometry with the plasmons induced on the gold surface, our 2D IR spectrometer was able to measure a monolayer of proteins and enhance the 2D IR signal by 20,000 times. The SEAR technique combines two new technologies in the field into one to provide 2D IR spectroscopy the means to enhance the signal from a monolayer of molecules on a surface.

A.3 ISOLATING SIGNALS FROM MOLECULES AT SURFACES

The second part of my PhD work also relies on controlling the polarization of light used in our experiment to observe signals that are specific to molecules at the surface. For example, if our system included both bulk molecules that are in a solution and some molecules that are oriented on the surface (Fig. A.2B), the proposed technique would only interrogate the molecules oriented

on the surface. We term the method singular cross-polarized 2D spectroscopy and it is accomplished by a stringent choice of the polarization of light used in the experiment.

We found a specific polarization condition of our light that uniquely measures signals from the interaction of the light with the molecules at the surface. Specifically, by controlling the polarization, the resulting 2D spectrum contains only cross-peak signals from oriented molecules at the surface (Fig. A.9A). In the singularly cross-polarized method, the pump and probe pulses are polarized in the same direction before they hit the sample. Then, after the sample, we place a polarizer (like our sunglasses) in the path of the signal and probe light. We turn the polarizer to select for the perpendicular direction of that initial polarization. For example, the pump and probe pulses may be vertically polarized, while the polarizer after the sample is set to select for the

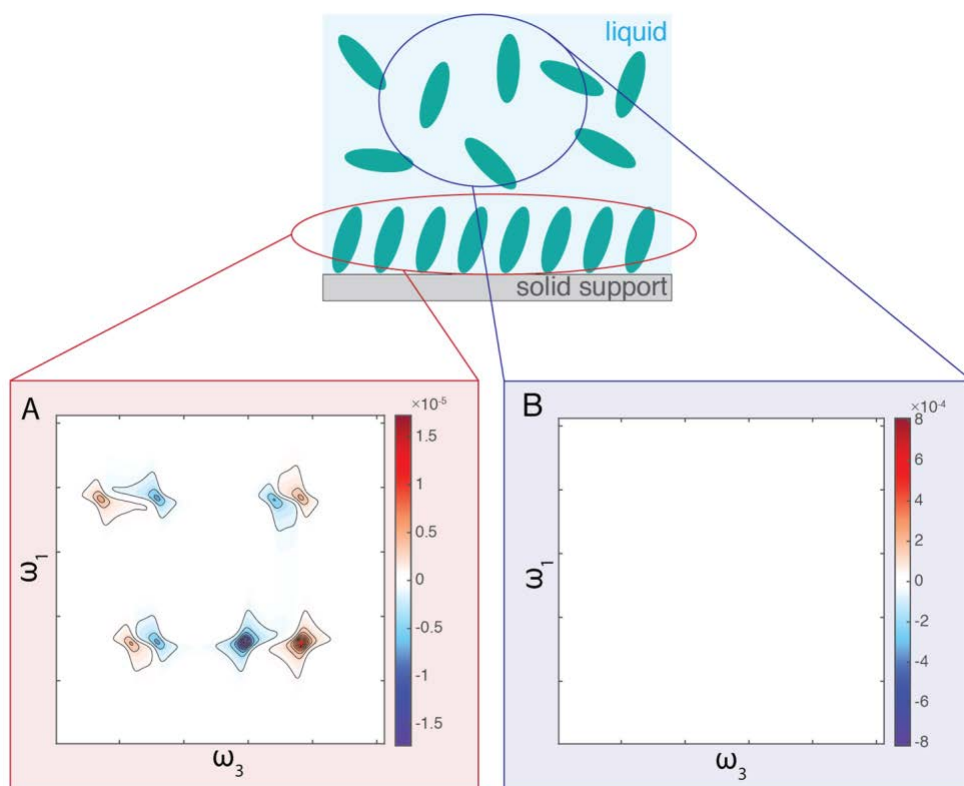


Figure A.9 The 2D spectra observed from A) surface molecules and B) bulk molecules when a singularly cross-polarized technique is used.

horizontal direction, or vice versa. The signals of these same molecules in a solution are zero under

these polarization conditions (Fig. A.9B) and do not contribute to the observed signal. Thus, by using the singularly cross-polarized technique, signals from molecules at the surface can be probed specifically. This type of information has not been attainable by other 2D IR and 2D white-light spectroscopies and expands the types of systems that could be measured by 2D spectroscopists. I worked on developing the theoretical foundation of this singularly cross-polarized technique and was able to show the success of the technique experimentally on an ideal system of molecular crystals.

A.4 CONCLUSION

Often while working in the lab and performing experiments where I am manipulating the polarization of light, I think back to my days at the beach, and the natural phenomenon of sunlight interacting with the water. The fundamental ways in which light touches our world are relevant to both how we see the world and how we can learn about that world at a molecular level. In my research, I have relied on these fundamental properties of light to glean information on surfaces and open up the possibility for more experiments in the field of 2D spectroscopy.